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Antiseptic film

[Claims]

1. An antiseptic film consisting of a hydrophilic polymer film containing an antiseptic zeolite.

2. The antiseptic film according to Claim 1 wherein the content of the zeolite is 10-300 mg per 1 m^2.

3. The antiseptic film according to Claim 1 wherein the average particle diameter of the antiseptic zeolite is 0.3-6μ m.

4. An antiseptic multiple layer sheet consisting of a support and a hydrophilic polymer film of a thickness of less than 20μ m or less and provided on one or both surfaces of the support, said film containing an antiseptic zeolite.

[0001]

[Field of industrial utilization]

The present invention relates to a hydrophilic polymer film containing an antiseptic zeolite, and more particularly to a packaging material for preserving freshness of foods which excels in anti-droplet property and transparency, and to a film having both antistatic and antiseptic properties utilizing the nature of not acquiring electrostatic charges.

[0002]

[Prior art]

It is known in the art that polymer films containing a porous fine powder such as activated charcoal, silica gel or alumina kneaded therein were used as films for preserving freshness of vegetables or fruits. However, they took merely into consideration removal of ethylene gas which is a kind of growth hormone or moisture which is often a cause of perishing and their effect of preserving the freshness was not sufficient.

[0003]

On the other hand, there is a trial of kneading an antiseptic agent directly into a polymer film. Particularly, there is a proposal to apply a highly safe antiseptic zeolite to an organic polymer film to impart the film an antiseptic property (JP 64-6031 A). The film containing antiseptic zeolite itself has a high antiseptic property and accordingly is one of superior packaging materials for foods or the like. However,

when polymers from petroleum such as polyethylene and polypropylene, which are commonly used in the packaging industry in a great amount, are used, they are hydrophobic and condensed water is apt to deposit on the inside surface of the package and thus the contents becomes difficult to see through the film. In addition, these polymers derived from petroleum require antistatic treatment, leading to defect of losing antiseptic property.

[0004]

Accordingly, the present invention aims at providing an antiseptic film having excellent anti-droplet property, transparency, and anti-electrostatic property. Further object of the invention is to provide an antiseptic multiple layer sheet containing such antiseptic film.

[0005]

In light the above-mentioned problems, the present inventor conducted an extensive study and has found that a film of polymer having a number of hydrophilic groups such as cellophane and sodium polyacrylate and antiseptic zeolite incorporated in the polymer is an excellent packaging material which does not decrease the anti-electrostatic property but has a superior anti-droplet property.

[0006]

The antiseptic film according to the present invention consists of a hydrophilic film containing antiseptic zeolite. The present invention will be explained in detail in the following. As the zeolite, naturally occurring and synthetic zeolites may be used. Zeolite is an aluminosilicate having a three dimensional skeleton structure, expressed by the general formula: $XM_{2/3}Al_2O_3YSiO_2ZH_2O$ where M is ion-exchangeable metal ion, n is valency of the metal ion, X and Y are numbers of silica and crystal water, respectively. Examples of zeolite are A-type zeolite, X-type zeolite, Y-type zeolite, T-type zeolite, high silica zeolite, sodalite, mordenite, analcite, clinoptilolite, chabasite, elionite may be cited but not limited to them.

[0007]

The particle diameter of zeolite used in the present invention is preferably in the range of 0.3-6μ m from the aspect of improving dispersability of the antiseptic zeolite, and enhancing the transparency and the antiseptic property. The zeolite usable in the present invention is prepared by replacing a part or all of ion-exchangeable ions in the zeolite such as sodium ions, calcium ions, potassium ions, magnesium ions, or iron ions with antiseptic metal ions.

[0008]

In the present specification, % means weight % on 110°C dry basis. In the following, process of preparing antiseptic zeolite used in the present invention will be explained. For example, the antiseptic zeolite used in the present invention is

prepared by contacting zeolite with an aqueous mixture solution of antiseptic metal ions such as silver ions, cupper ions, zinc ions, tin ions to replace the ion-exchangeable ions in the zeolite with the antiseptic metal ions. The contact is performed at 10-70 ℃, preferably 40-60 ℃, for 3-24 hours, preferably 10-24 hours in batch or on continuous (using column) basis. pH is adjusted to 3-10, preferably 5-7. By this adjustment, deposition of the silver oxide and the like on the surface as well as in the inside of the zeolite can be desirably prevented. Ions in the mixture aqueous solution are usually supplied as salts. For example, silver ions are supplied as silver salt such as silver nitrate, silver sulfate, silver perchlorate, silver acetate, diamine silver nitrate, diamine silver sulfate; cupper ions are supplied as cupper (II) nitrate, cupper sulfate, cupper perchlorite, cupper acetate, potassium tetracyano cuprate; zinc ions are supplied as zinc (II) nitrate, zinc sulfate, zinc perchlorate, zinc thiocyanate, zinc acetate; and tin ions are supplied as tin sulfate, tin nitrate.

[0009]

The quantities of silver ions and others in the zeolite may be appropriately adjusted by adjusting the concentration of respective ions (salts). For example, if the antiseptic zeolite contains silver ions, the concentration of the silver ions in the aqueous solution may be selected within the range of 0.002-0.15 M/liter so that antiseptic zeolite having silver ion content of 0.5-5 % can be obtained. If the antiseptic zeolite further contains cupper ions or zinc ions, the concentration of cupper ions or zinc ions in the solution may be selected within the range of 0.1-2.3 M/liter or 0.15 -2.8 M/litter, respectively so that antiseptic zeolite having cupper or zinc ion content of 0.1-18% or 0.1-18%, respectively, can be obtained.

[0010]

In order to prevent the antiseptic zeolite of the present invention from discoloration, a part of the ion-exchangeable ions in the zeolite may be ion-exchanged with ammonium ions and amine ions. Preferable amount of addition of ammonium ions and amine ions is 0.4-3%. In the present invention, ion exchange may be performed by preparing aqueous solutions of respective ions in addition to the mixture solution and the zeolite is ion-exchanged with each aqueous solution one after another. The concentration of each solution may be selected in proportion to the concentration of each type of ions in the mixture solution.

[0011]

The resulting ion-exchanged zeolite is sufficiently washed with water and dried. The drying operation is preferably effected at 105-115℃ under the normal pressure or at 70-90℃ under reduced pressure (1-30 torr). The hydrophilic polymer has a number of hydrophilic groups such as hydroxyl group, carboxyl group, amino group, sulfonic

group, ketone group etc. and has a film-forming property. For example, cellophane, modified cellulose, gelatin, chitosan, polyvinyl alcohol, polyethylene oxide, polysodium acrylate may be cited.

[0012]

The antiseptic film according to the present invention may be obtained by blending the above-described antiseptic zeolite with the above-described hydrophilic polymer solution according to the conventional method, and extruding the blend through a die into a film, or additionally chemically reacting the resulting film. The film production is carried out, in the case of cellophane for example, by extruding a viscose (α -cellulose content:9.5%) of a constant degree of aging from a slit of 160μ m into a solidifying bath containing 14% of sulfuric acid and 15% of sodium sulfate maintained at 40°C to solidify the viscose, passing the extruded viscose through a 5% sulfuric acid solution to regenerate cellulose, subsequently leading it to a solution containing 0.2% of caustic soda and 0.2% of sodium sulfate at 60°C to remove the byproduct sulfur in the cellophane, treating it with a solution containing 0.1% of sodium hypochlorite to remove the colored components, fully washing it, treating it with a glycol solution for imparting flexibility and drying it with a cylinder to obtain a cellophane film.

[0013]

The antiseptic film preferably has a thickness of 20μ m or less. The content of the antiseptic zeolite in the antiseptic film is suitably 10-300mg/m^2 to obtain transparency of the antiseptic film. The present invention further provides a multiple layer antiseptic sheet consisting of the antiseptic film supported on one or both surfaces of a support. Such support may be a resin film of hydrophobic resin such as ionomer resin, EEA resin, EVA resin, vinylchloride resin, vinylidenechloride resin, chlorinated polyethylene, fluorinated resin, polyamide resin, polyetherketone, polysulfone, polyethylene, polycarbonate, polybutadiene, polypropylene, polystyrene, polyacrylate, polyurethane, polyethylene terephthalate; or of hydrophilic resin such as cellophane, modified cellulose, gelatin, chitosan, polyvinylalcohol, polyethylene oxide, polysodiumacrylate. The thickness of the support may vary depending on application and strength, but has a thickness of, for example, 5-100μ m, and preferably 10-50 μ m.

[0014]

As method for forming the antiseptic film on one or both surfaces of a support, air

doctor, plate coater, rod coater, bar coater, knife coater, squeeze coater, reverse coater, transfer coater, gravure coater, kiss-roll coater, cast coating, spray coating, calendar coating and dipping may be cited.

[0015]

The antiseptic film of the present invention has a thickness of 20μ m or less and excels in droplet-proof property and transparency, and can be used, for example, as food packaging material, container for foods, packaging material for medical use, packaging material for clothing.

[0016]

(Effect of the invention)

The antiseptic film has an appropriate water-absorbing property as well as anti-electrostatic property, and accordingly excels in droplet-proof and anti-electrostatic properties and transparency when applied to packaging of various materials.

[0017]

(Example)

Mode of working of the invention will be described in connection with examples, but is not restricted to the examples.

Referential Example (Preparation of antiseptic zeolite)

Two types of commercially available zeolites, namely, A-type zeolite ($Na_2O \cdot Al_2O_3 \cdot 2.0SiO_2 \cdot H2O$: average diameter 4.3μ m) and Y-type zeolite($Na_2O \cdot Al_2O_3 \cdot 4.0SiO_2 \cdot XH2O$: average diameter 0.7μ m) were used. $AgNO_3$、$Zn(NO_3)_2$ and NH_4NO_3 were used for supplying respective ions.

[0018]

In Table 1, types of zeolites used in the preparation of the samples and the salts and their concentration in the mixture solution are listed. Four samples, Nos. 1 to 4, of antiseptic zeolites were prepared. For each sample, 1 kg of the zeolite powder dried at 110℃ was weighed and dispersed in 1 litter of water and 0.05N aqueous solution of nitric acid was dripped at a rate of 100 ml/30 minutes to adjust the solution to a given pH value(5-7). Thereafter, 3 litters of a mixture solution of an antiseptic metal salt having a predetermined concentration to the slurry for ion exchange. This reaction was carried out at 6℃ for 10-24 hours with agitation until equilibrium condition is reached.

[0019]

After the ion exchange was completed, zeolite phase was filtered out and washed

with water at ambient or warmed temperature until the excess exchange cations were removed. Then, the sample was heated to 110℃ for drying and thus four types of samples were obtained.

【0020】

[Table 1]

No.	Zeolite type	Contents in Zeolite (%) Ag	Zn	Ammonium	Yield(g)	Solution concentration (mol/l) $AgNO_3$	$Zn(NO_3)_2$	NH_4NO_3
1	A	2.5	14.0	1.2	960	0.06	2.0	1.4
2	A	5.0	---	3.1	960	0.11	---	1.8
3	A	13.8	---	---	940	0.40	---	---
4	Y	3.5	7.1	0.9	950	0.08	1.0	1.2

[0021]

Example 1

A given amount of the antiseptic zeolite obtained in Referential Example was added to 100 parts of a stable viscose having a degree of aging (HZ value: 7) and sufficiently agitated to obtain a homogeneous dispersion and thereafter degassed under a reduced pressure. The mixture was extruded through a slit of 160μ m into a solidifying bath containing 14% of sulfuric acid and 15% of sodium sulfate maintained at 40℃ to solidify the viscose, passing the extruded viscose through a 5% sulfuric acid solution to regenerate cellulose, subsequently leading the same to a solution containing 0.2% of caustic soda and 0.2% of sodium sulfate at 60℃ to remove the byproduct sulfur in the cellophane, treating it with a solution containing 0.1% of sodium hypochlorite to remove the colored components, fully washing it, treating it with a glycol solution for imparting flexibility and drying it with a cylinder to obtain a cellophane film of a thickness of 20μ m. Films having similar droplet-proof property were prepared in the similar manner except that the antiseptic zeolite was added to hydrophobic polymer (Comparative Example 1-1) and silica gel was used in place of the antiseptic zeolite (Comparative Example 1-2). The conditions of production are shown in Table 2.

[0022]

Example 2

A give amount of the antiseptic zeolite obtained in Referential Example was added to 100 parts of aqueous solution of 5% sodium alginate (manufactured by Kimizuka

Chemical K.K.) and sufficiently agitated until a homogeneous dispersion is obtained and then degassed under a reduced pressure. The mixture liquid was extruded through a slot of 240 μ m into an aqueous solution of 10% calcium chloride to solidify the extruded mixture which was, in turn, dried on a cylinder under tension, whereby a sodium alginate film having a film thickness of 15μ m was obtained. Films having similar droplet–proof property were prepared in the similar manner except that the antiseptic zeolite was added to hydrophobic polymer (Comparative Example 2-1) and alumina was used in place of the antiseptic zeolite (Comparative Example 2-2). The conditions of production are shown in Table 2.

[0023]

Table 2

	No.	Antiseptic zeolite No.	Hydorphilic polymer	Antiseptic zeolite in final product
Example	1-1	1	Cellophane	157 (mg/m^2)
	1-2	1	Cellophane	293
	1-3	3	Cellophane	10
	2-1	2	Sodium alginate	103
	2-2	4	Sodium alginate	122
	2-3	4	Sodium alginate	87
Comp. Example	1-1	1	Polyethylene	158
	1-2	Silicagel	Cellophane	855
	2-1	2	Polyethylene	112
	2-2	Alumina	Sodium alginate	807

[0024]

Example 3

A given amount of the antiseptic zeolite obtained in the Referential Example was added to 10% aqueous solution of polyvinylalcohol (manufactured by Kuraray) and sufficiently agitated to obtain a homogenous dispersion and then degassed under a reduced pressure. The mixture liquid was coated on a support using a bar coater, dried at 100℃ for 3 minutes to obtain a laminate sheet. As examples, those containing no antiseptic zeolite were also produced in a similar manner (Comparative Examples 3,4). The production conditions are shown in Table 3.

[0025]

Table 3

No.		Anticeptic zeolite No.	Support material	Antiseptic zeolite in final product (mg/m2)
Example	3-1	1	Cellophane 20μm	56.2
	3-2	4	Polyethylene 10 μm	10.8
Comp. Example	3	---	Cellophane 20μm	---
	4	---	Polyethylene 10 μm	---

[0026]

[Test 1] (antiseptic test)

The antiseptic properties of the resulting antiseptic films were evaluated according to the following procedure. As a test strain, yellow MRSA (methicillin-resistant staphylococcus aureus) was used. The bacterial liquid was incubated at 38℃ for 18 hours on a conventional agar culture and adjusted the number of bacteria to 1045 per 1 m^2 by using sterilized physiological saline. On each of 50mmx50mm of the antiseptic films, 1 ml of the bacterial liquid was splayed and preserved at 37℃ for 24 hours. The bacteria was washed out from the surface of the film and the viable bacteria was count ed. The result of viable counts is shown in Table 4.

[0027]

[Test 2] (droplet-proof property, wetting property, and transparency)

The droplet-proof property was measure by leaving the surface of each film wetted with water for 1 minute as it stands and then the presence of repelled water was evaluated according to the following criteria.

○ Water covers the film surface and repellency is not observed

△ Water covers the film surface but the water film is broken within 1 minute.

× Water is repelled and droplets appear on the film surface.

[0028]

The wetting property was evaluated by placing and leaving each film on a beaker containing 200 ml of warm water at 55-60℃ for 20 minutes and judging based on the following criteria.

○ Substantially no water is observed on the film.

△ Large water droplets are sporadically observed on the film surface and the inside of the beaker is hard to see through.

× Large number of water droplets are deposited and the inside of the beaker cannot be seen through.

[0029]

The transparency was evaluated on each film of 40μ m, using NDH-20D haze meter (manufactured by Nihon Denshoku) and light transmission ratio measurement was effected in the entire visible range using 200-20 spectrophotometer(manufactured by Hitachi Limited). The results are shown in Table 4.

[0030]

Table 4

	No.	Antiseptic Bacteria count	Water repellance	Wettability	Transparency Hazemeter	Transparency Transmissivity (%)
Example	1-1	0 (/ml)	○	○	3.0	83.0
	1-2	0	○	○	2.8	81.5
	1-3	0	○	○	2.6	82.6
	2-1	0	○	○	2.8	83.1
	2-2	0	○	○	2.5	83.6
	2-3	0	○	○	2.8	82.5
	3-1	0	○	○	2.4	86.5
	3-2	0	○	○	2.2	88.7
Comp. Example	1-1	0	△	△	3.0	84.0
	1-2	1×10^4	○	○	27.6	57.0
	2-1	0	△	×	2.6	82.6
	2-2	3×10^4	○	○	29.8	53.7
	3	3×10^4	○	○	2.2	84.6
	4	6×10^4	○	○	2.4	87.6